

# Net Charge on a Noble Gas Atom Adsorbed on a Metallic Surface

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Adsorbed noble gas atoms donate (on the average) a fraction of an electronic charge to the substrate metal. The effect has been experimentally observed as an adsorptive change in the electronic work function. The connection between the effective net atomic charge and the binding energy of the atom to the metal is theoretically explored.

PACS: 73.30.+y, 34.50.Dy, 68.10.Gw

## I. INTRODUCTION

The problem of measuring and understanding the binding energy of noble gas atoms on metal substrates has always been of considerable interest [1–6]. The atomic binding is that energy released when an atom from the vapor sticks to the surface. Several studies have related atomic binding to surface charge distributions [1,7–15]. Induced surface electronic dipole moments near the adsorbed atom have been of particular interest. In the work which follows, the intimate relationship between binding energy and induced atomic charge will be considered in theoretical detail.

As the atom is lowered onto the surface and becomes adsorbed, the atomic dipole tends to be oriented with the positive side of the dipole pointing away from the metal. In reality, the negative side of the atomic dipole is better thought to be *on average* an electron (negative) charge  $-Z_{eff}|e|$  donated to the metal. This leaves the atom with a positive net mean charge  $+Z_{eff}|e|$ . The physical situation is pictured in FIG.1 below. Even in a situation often regarded as physisorption, one does not expect a noble gas atom to remain in perfect charge neutrality. When the atom is adsorbed on the substrate, the negative end of the atomic dipole moment neutralizes the positive end of the *image* dipole moment. This leaves a mean net positive charge on the atom and a mean negative electronic charge deposited in the metal. From an experimental viewpoint, the positive nature of the mean charge on an adsorbed noble gas atom is equivalent to the donation of a negative charge to the metal. The physical effect is

made manifest [1–3,9–14,16,18] by the diminution of the electronic work function as the first monolayer of atoms is deposited on the metallic substrate surface. This effect is quite large and is observed for all combinations of gases and metals [7]. The magnitude of the reduction of the work function is proportional to the amount of adsorbate and for coverage up to a monolayer [15].

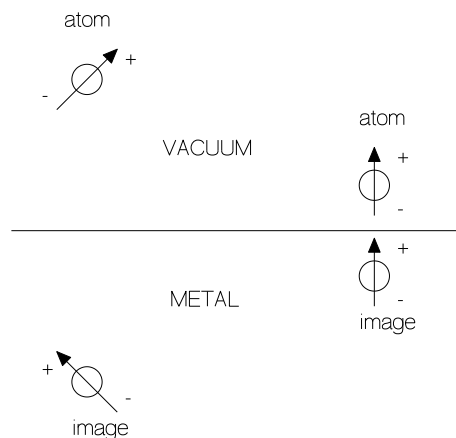


FIG. 1. Shown is the surface between the vacuum and the metal. When an atom is far above the surface between the vacuum and the metal the dipole fluctuations are correlated with the image dipole, as shown to the left. As the atom is lowered onto the surface, the atomic dipole is pointed upwards as shown on the right. An electron is then donated to the metal with probability giving the effective charge strength  $Z_{eff}$ .

In Secs. II and III the long ranged part of Van der Waals interaction between a noble gas atom and a metal will be reviewed. The height of the atom, over and above the metal surface, is considered to be large compared with the atomic size. The interaction is between a quantum fluctuating dipole and its correlated image. Both

the binding energy and the probability of electronic excitation will be computed numerically in Sec. IV. In Sec. V, non-perturbative expressions for the binding energy and the probability of electronic excitation are derived. In Sec. VI it is shown that the stronger the binding energy the larger the net atomic adsorptive charges. The physical importance of the adsorptive charge on a noble gas atom is discussed in the concluding Sec. VII.

## II. PERTURBATION THEORY

Suppose a Hamiltonian of the form

$$\mathcal{H} = H + V, \quad (1)$$

in which

$$H\psi_n = E_n\psi_n, \quad (2)$$

represents an unperturbed energy eigenvalue problem, and

$$\mathcal{H}\Psi_n = \mathcal{E}_n\Psi_n, \quad (3)$$

represents the perturbed energy eigenvalue problem. Without loss of generality, one may assume (for the unperturbed ground state wave function) that

$$(\psi_0, V\psi_0) = 0. \quad (4)$$

Two quantities of importance are the exact ground state energy  $\mathcal{E}_0$ , and the probability that the interaction  $V$  introduces an excitation in the unperturbed quantum states

$$P = \sum_{n \neq 0} |(\psi_n, \Psi_0)|^2 = 1 - |(\psi_0, \Psi_0)|^2. \quad (5)$$

In lowest order perturbation theory, one then finds the energy shift [19]

$$U = (\mathcal{E}_0 - E_0) = - \sum_{n \neq 0} \frac{|(\psi_n, V\psi_0)|^2}{(E_n - E_0)} + \dots, \quad (6)$$

The ground state wave function in first order perturbation theory [20] is given by

$$\Psi_0 = \psi_0 - \sum_{n \neq 0} \frac{(\psi_n, V\psi_0) \psi_n}{(E_n - E_0)} + \dots. \quad (7)$$

The first order wave equation can be used to compute the excitation probability  $P$  to second order in the perturbation potential; it is

$$P = \sum_{n \neq 0} \left| \frac{(\psi_n, V\psi_0)}{(E_n - E_0)} \right|^2 + \dots. \quad (8)$$

Let us apply these ideas to the Casimir effect, i.e. the attractive force on an atom located at height  $h$  above a metallic substrate. The final energy is well known. However, the excitation probability of the atom will also be calculated.

## III. THE VAN DER WAALS FORCE

Let the unperturbed problem consist of an isolated atom and an isolated metal

$$H = H_{atom} + H_{metal}. \quad (9)$$

With  $n = (j, a)$  as a double index referring to the atomic state  $j$  and the metallic substrate state  $a$ , we may write

$$\psi_n = \psi_j^{atom} \psi_a^{metal}, \quad (10)$$

with an unperturbed energy

$$E_n = E_j^{atom} + E_a^{metal}. \quad (11)$$

Further, let the interaction between the atom and metal be of the dipole form

$$V = -\mu \cdot \mathbf{E} \quad (12)$$

where  $\mu$  represents the atomic electric dipole moment operator, and the electric field  $\mathbf{E}$  is produced by the metal. The second order perturbation interaction energy between the atom and the metal is usually called the Casimir effect and is given by

$$U_C = - \sum_{(a,j) \neq (0,0)} \frac{|\mu_{j0} \cdot \mathbf{E}_{a0}|^2}{(\hbar\omega_{j0} + \hbar\omega'_{a0})}, \quad (13)$$

where

$$\mu_{j0} = (\psi_j^{atom}, \mu \psi_0^{atom}), \quad (14)$$

and

$$\mathbf{E}_{a0} = (\psi_a^{metal}, \mathbf{E} \psi_0^{metal}). \quad (15)$$

The atomic Bohr frequencies are defined as

$$\hbar\omega_{j0} = (E_j^{atom} - E_0^{atom}). \quad (16)$$

and the metallic Bohr frequencies are defined as

$$\hbar\omega'_{a0} = (E_a^{metal} - E_0^{metal}). \quad (17)$$

For an isotropic atom, one may define a ground state dipole moment quantum noise spectral function

$$S(\omega) = \frac{1}{3} \sum_{j \neq 0} |(\psi_j^{atom}, \mu \psi_0^{atom})|^2 \delta(\omega - \omega_{j0}), \quad (18)$$

Similarly, one may define the electric field quantum zero point fluctuations due to the metal

$$S_{\mathbf{E}}(\omega') = \sum_{a \neq 0} |(\psi_a^{metal}, \mathbf{E} \psi_0^{metal})|^2 \delta(\omega' - \omega'_{a0}). \quad (19)$$

One may now compute the Casimir energy [21–23]  $U_C$  in terms of these spectral functions; i.e.

$$U_C = - \left( \frac{1}{\hbar} \right) \int_0^\infty \int_0^\infty \left( \frac{S(\omega) S_{\mathbf{E}}(\omega')}{\omega + \omega'} \right) d\omega d\omega'. \quad (20)$$

Finally, one may find the spectral functions by employing the zero point quantum fluctuation response theorems [24].

For example, if the atomic polarization response to an external electric field at complex frequency  $\zeta$  (with  $\Im m(\zeta) > 0$ ),

$$\delta \langle \mu \rangle = \alpha(\zeta) \delta \mathbf{E}_{ext}, \quad (21)$$

defines the ground state atomic polarizability  $\alpha(\zeta)$  for a spherical atom, then the fluctuation response theorem asserts

$$S(\omega) = \left( \frac{\hbar}{\pi} \right) \Im m \alpha(\omega + i0^+). \quad (22)$$

The fluctuation spectral function for the electrostatic field  $\mathbf{E} = -\nabla\phi$  produced by the metal is a bit more subtle.

If an external charge density at complex frequency  $\zeta$  produces an electrostatic potential according to the rule

$$\delta \langle \phi(\mathbf{r}) \rangle = \int \mathcal{G}(\mathbf{r}, \mathbf{r}', \zeta) \delta \rho_{ext}(\mathbf{r}') d^3 \mathbf{r}', \quad (23)$$

then the spectral function for zero point electrostatic potential fluctuations

$$S_\phi(\mathbf{r}, \mathbf{r}', \omega) = \int_{-\infty}^{\infty} \cos(\omega t) \Re e \langle 0 | \Delta \phi(\mathbf{r}, t) \Delta \phi(\mathbf{r}', 0) | 0 \rangle \left( \frac{dt}{2\pi} \right) \quad (24)$$

obeys the fluctuation response theorem in the form

$$S_\phi(\mathbf{r}, \mathbf{r}', \omega) = - \left( \frac{\hbar}{\pi} \right) \Im m \mathcal{G}(\mathbf{r}, \mathbf{r}', \omega + i0^+). \quad (25)$$

For the problem at hand, suppose that the metal is located in the half-space  $z < 0$ ; e.g. the substrate surface is the  $z = 0$   $x$ - $y$  plane. If both  $\mathbf{r}$  and  $\mathbf{r}'$  are in the vacuum (i.e.  $z > 0$  and  $z' > 0$ ), then the “method of images” yields the Greens function

$$\mathcal{G}(\mathbf{r}, \mathbf{r}', \zeta) = \left( \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right) - \left( \frac{\eta(\zeta)}{|\mathbf{r} - \mathbf{r}'_i|} \right), \quad (26)$$

where

$$\mathbf{r}' = (x', y', z'), \quad (27)$$

has a corresponding “image” position

$$\mathbf{r}'_i = (x', y', -z'), \quad (28)$$

and

$$\eta(\zeta) = \left( \frac{\varepsilon(\zeta) - 1}{\varepsilon(\zeta) + 1} \right). \quad (29)$$

The dielectric response function for the metal  $\varepsilon(\zeta)$  determines the conductivity  $\sigma(\zeta)$  via

$$\varepsilon(\zeta) = 1 + \left( \frac{4\pi i \sigma(\zeta)}{\zeta} \right). \quad (30)$$

Thus

$$S_\phi(\mathbf{r}, \mathbf{r}', \omega) = \left( \frac{\hbar}{\pi |\mathbf{r} - \mathbf{r}'_i|} \right) \Im m \eta(\omega + i0^+). \quad (31)$$

With

$$\mathbf{R} = (0, 0, h) \quad (32)$$

denoting the position of the atom at a height  $h$  above the substrate surface, the electric field zero point fluctuations of the electric field at the atom may be computed via

$$S_{\mathbf{E}}(\omega) = \lim_{\mathbf{r} \rightarrow \mathbf{R}} \lim_{\mathbf{r}' \rightarrow \mathbf{R}} \left( \frac{\partial^2}{\partial x \partial x'} + \frac{\partial^2}{\partial y \partial y'} + \frac{\partial^2}{\partial z \partial z'} \right) S_\phi(\mathbf{r}, \mathbf{r}', \omega). \quad (33)$$

The differentiation is tedious but direct. It yields

$$S_{\mathbf{E}}(\omega) = \left( \frac{\hbar}{2\pi} \right) \left( \frac{\Im m \eta(\omega + i0^+)}{h^3} \right). \quad (34)$$

Substituting Eqs.(22) and (34) into Eq.(20) yields the zero-point fluctuation Casimir effect potential

$$U_C = - \left( \frac{C_{atom}}{h^3} \right) \quad (35)$$

where

$$C_{atom} = \left( \frac{\hbar}{2\pi^2} \right) \times$$

$$\int_0^\infty \int_0^\infty \left( \frac{\Im m \alpha(\omega + i0^+) \Im m \eta(\omega' + i0^+)}{\omega + \omega'} \right) d\omega d\omega'. \quad (36)$$

The Casimir form of the Van der Waals potential between an atom and a conducting surface is well known. The purpose for reviewing the Van der Waals result is that now we may also calculate the probability that the atom at a height  $h$  is in an excited state.

The excited state probability in Eq.(5), when evaluated to the lowest order perturbation theory in Eq.(8), yields the Casimir excited state probability  $P_C$ . In the Casimir perturbation theory, the probability for the atom to be in an excited state contains an extra energy denominator. The final result is in the simple form

$$P_C = \left( \frac{v_{atom}}{h^3} \right). \quad (37)$$

The parameter  $v_{atom}$  is a rough measure of the effective atomic volume; It is

$$v_{atom} = \left( \frac{1}{2\pi^2} \right) \times \int_0^\infty \int_0^\infty \left( \frac{\Im m \alpha(\omega + i0^+) \Im m \eta(\omega' + i0^+)}{(\omega + \omega')^2} \right) d\omega d\omega'. \quad (38)$$

The excited state probability in Eq.(37) is a new result. The noble gas atom above the metal, is *not* electronically inert. The atom in the vacuum is in the ground state, As the atom is lowered toward the metal surface, the atomic electronic state becomes excited with probability  $P > 0$ . For heights  $h$  such that  $h^3 \gg v_{atom}$  we have  $P \approx P_C$  as in Eq.(37). Numerical results for the probability  $P_C$  then follow (below) in a similar manner to numerical results for  $U_C$  which have been previously computed by other workers.

#### IV. NUMERICAL EVALUATIONS

For the purpose of numerical evaluations of parameters associated with the Van der Waals interaction, we follow Rauber, Klein, Cole and Bruch [25]; They choose a single pole approximation for both  $\alpha(\zeta)$  and  $\eta(\zeta)$ . The pole in  $\alpha(\zeta)$  is parameterized by an atomic frequency  $\omega_a$ , while the pole in  $\eta(\zeta)$  is parameterized by a plasma frequency  $\Omega_s$ .

In detail, the approximations read

$$\alpha^{RKC B}(\zeta) \approx \left( \frac{\omega_a^2 \alpha_0}{\omega_a^2 - \zeta^2} \right), \quad (39)$$

along with

$$\eta^{RKC B}(\zeta) \approx \left( \frac{\Omega_s^2 g_0}{\Omega_s^2 - \zeta^2} \right). \quad (40)$$

Eqs.(36), (38), (39) and (40) yield

$$C_{atom}^{RKC B} = \frac{\hbar}{8} \left\{ \frac{\alpha_0 g_0 \omega_a \Omega_s}{\omega_a + \Omega_s} \right\}, \quad (41)$$

and

$$v_{atom}^{RKC B} = \frac{1}{8} \left\{ \frac{\alpha_0 g_0 \omega_a \Omega_s}{(\omega_a + \Omega_s)^2} \right\}. \quad (42)$$

The values of the atomic parameters  $\alpha_0$  and  $\omega_a$  have been previously tabulated [25]. and are listed in Table I. The values of  $g_0$  and  $\Omega_s$ , (for several metals) have also been previously tabulated [25] and are here listed in Table II. In Table III, we have computed the values of  $C_{atom}$  and  $v_{atom}$ .

The probability of atomic excitation in the Casimir regime  $P_C = (v_{atom}/h^3)$  can be calculated in the limit of

large  $h$ . When the height of the atom obeys  $h^3 \gg v_{atom}$ , the perturbation theory is reliable. However, for atoms adsorbed on a submonolayer of film the height  $h$  is not large. Thus a non-perturbative method is required. We now turn our attention to this more detailed treatment.

TABLE I. Values of  $\alpha_0$  and  $\hbar\omega_a$  for Noble gas atoms.

Atom	$(\alpha_0/\text{\AA}^3)$	$(\hbar\omega_a/\text{eV})$
He	0.205	27.645
Ne	0.396	32.734
Ar	1.642	18.971
Kr	2.487	16.478
Xe	4.018	14.34

TABLE II. Values of  $g_0$  and  $\hbar\Omega_s$  for some metals.

Atom	$(g_0)$	$(\hbar\Omega_s/\text{eV})$
Cu	0.857	17.74
Ag	0.812	21.768
Au	0.840	24.162
Al	0.976	12.87
Pd	0.785	17.115
Gr	0.619	18.149

TABLE III.  $C_{atom}$  and  $v_{atom}$  for noble gas atoms.

Gas-Metal	$(C_{atom}/\text{\AA}^3 \text{eV})$	$(v_{atom}/\text{\AA}^3)$
Xe-Cu	3.413	0.106
Xe-Ag	3.525	0.098
Xe-Au	3.797	0.099
Kr-Cu	2.276	0.067
Kr-Ag	2.367	0.062
Kr-Au	2.558	0.063
Ar-Cu	1.612	0.044
Ar-Ag	1.690	0.041
Ar-Au	1.832	0.043
Ne-Cu	0.488	0.096
Ne-Ag	0.525	0.096
Ne-Au	0.578	0.010
He-Cu	0.237	0.005
He-Ag	0.253	0.005
He-Au	0.277	0.005

## V. RIGOROUS RESULTS

The above considerations are true for atoms above a metal in the perturbative limit  $\hbar \rightarrow \infty$ . When the atom is adsorbed on the metal surface, a non-perturbative viewpoint must be invoked [26,27]. For example, consider the ground state matrix element analytic in the upper half complex energy plane  $\Im m z > 0$ ,

$$G(z) = \left( \psi_0, \left\{ \frac{1}{z - \mathcal{H}} \right\} \psi_0 \right), \quad (43)$$

where  $\psi_0$  is the unperturbed ground state,

$$H\psi_0 = E_0\psi_0, \quad (44)$$

and the binding energy of the adsorbed atom,

$$U = -B, \quad B > 0, \quad (45)$$

is determined by the full electronic ground state

$$\mathcal{H}\Psi_0 = (H + V)\Psi_0 = (E_0 + U)\Psi_0. \quad (46)$$

One may write Eq.(43) in the exact form

$$G(z) = \left\{ \frac{1}{z - E_0 - \Sigma(z)} \right\}, \quad (47)$$

where the self energy part  $\Sigma(z)$  determines the atomic binding energy

$$U = \Sigma(E_0 + U). \quad (48)$$

$G(z)$  has a simple pole at the exact ground state energy  $z_0 = E_0 + U = E_0 - B$ . The residue at the pole is the transition probability  $\psi_0 \rightarrow \Psi_0$ ; i.e.

$$|(\Psi_0, \psi_0)|^2 = \left( \frac{1}{1 - \Sigma'(E_0 + U)} \right), \quad (49)$$

where  $\Sigma'(z) = d\Sigma(z)/dz$ . The exact expression for the self energy part reads

$$\Sigma(z) = \left( \psi_0, V \left\{ \frac{1}{z - \mathcal{H}'} \right\} V \psi_0 \right), \quad (50)$$

where  $\mathcal{H}' = \hat{P}\mathcal{H}\hat{P}$  and where  $\hat{P}$  projects into the subspace normal to the unperturbed ground state. For example, from Eq.(49) and the definition of  $\hat{P}$  one finds the mean value  $P = (\Psi_0, \hat{P}\Psi_0)$  given by

$$P = 1 - |(\Psi_0, \psi_0)|^2 = \left( \frac{\Sigma'(E_0 + U)}{1 - \Sigma'(E_0 + U)} \right). \quad (51)$$

The details of the mathematical derivation of Eqs.(47)-(51) are given in the appendix.

Suppose that the atom (located on the metal surface) starts out in the unperturbed state  $\psi_0$ . The atom will then decay into its renormalized ground state, giving up

its excess binding energy  $U$  to the bulk electrons in the metal. The transition rate per unit time to deposit an electronic energy  $W$  to the metal is given by

$$\Gamma(W) = \left( \frac{2\pi}{\hbar} \right) (\psi_0, V\delta(E_0 + W - \mathcal{H}')V\psi_0). \quad (52)$$

From Eqs.(50) and (52) it follows that

$$\Sigma(z) = \left( \frac{\hbar}{2\pi} \right) \int_0^\infty \frac{\Gamma(W)dW}{z - (E_0 + W)}. \quad (53)$$

Thus the binding energy  $U = -B$  is rigorously determined by Eqs.(48) and (53) to be

$$B = \left( \frac{\hbar}{2\pi} \right) \int_0^\infty \frac{\Gamma(W)dW}{W + B}, \quad (54)$$

while Eqs.(51) and (53) imply

$$P = \left( \frac{\varpi}{1 + \varpi} \right), \quad (55)$$

where

$$\varpi = \left( \frac{\hbar}{2\pi} \right) \int_0^\infty \frac{\Gamma(W)dW}{(W + B)^2}, \quad (56)$$

In the perturbative limit,

$$\lim_{\hbar \rightarrow \infty} (P/P_C) = \lim_{\hbar \rightarrow \infty} (U/U_C) = 1 \quad (57)$$

where the Casimir values  $U_C$  and  $P_C$  have been defined, respectively, in Eqs.(35) and (37). For the non-perturbative limit of atomic adsorption for a finite height  $h = h_s$ , the exact results of Eqs.(54), (55) and (56) can be employed for making realistic estimates of the effective charge  $Z_{eff}|e|$  of the atom.

## VI. NET CHARGE ON AN ADSORBED ATOM

For estimating the effective charge on the adsorbed atom, we note the following: (i) Eq.(54) is an implicit equation for the binding energy  $B = f(B)$ . (ii) If  $\bar{\Gamma} = \lim_{W \rightarrow 0} \Gamma(W) > 0$ , then  $f(B \rightarrow 0) \approx (\hbar\bar{\Gamma}/2\pi)\ln(const/B)$ , where a constant ‘‘cut-off’’ must be placed in the logarithm. (iii) We employ the following simple dispersion formula for  $\Gamma(W)$ : Over a bandwidth  $0 < W < E_a$ , we consider  $\Gamma(W) = \bar{\Gamma}$  to be uniform. Outside this interval, i.e. for electronic energies above the atomic energy cut-off  $E_a = \hbar\omega_a$  in Table I, we consider  $\Gamma(W)$  to be negligible. Under this assumption, the binding energy Eq.(54) reads

$$B \approx \left( \frac{\hbar\bar{\Gamma}}{2\pi} \right) \ln \left( \frac{\hbar\omega_a}{B} \right), \quad (58)$$

if  $B \ll \hbar\omega_a$ . Similarly, Eq.(56) reads

$$\varpi \approx \left( \frac{\hbar \bar{\Gamma}}{2\pi B} \right), \quad (59)$$

The probability of excitation  $P = Z_{eff}$  determines the effective charge via Eqs.(55), (58) and (59)

$$Z_{eff} = \left( \frac{1}{1 + \ln(E_a/B)} \right). \quad (60)$$

A plot of the effective charge versus the binding energy is shown in Fig.2.

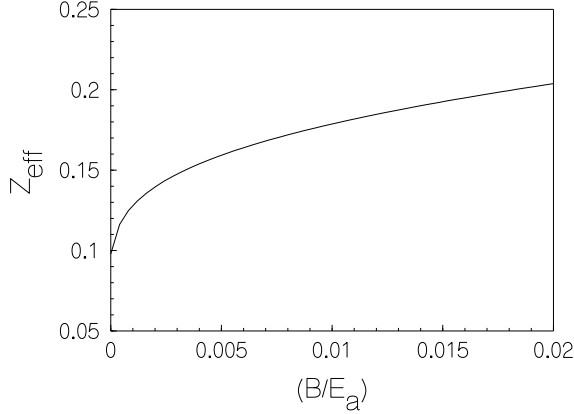


FIG. 2. The effective charge  $Z_{eff}|e|$  on the atom is shown as a function of the binding energy  $B$  in units of the atomic excitation energy  $E_a = \hbar\omega_a$ . See Table I.

In terms of experimental binding energies and mean atomic excitation energies listed Table I, the effective charges can be computed numerically from Eq.(60).

## VII. CONCLUSIONS

A dispersion theory has been presented for computing the effective charge per noble gas atom adsorbed on metallic substrates. The general physical situation, shown in Fig.1, is complimentary to the charge density functional approach for computing atomic binding. [28,29] Both approaches yield a picture in which there is an atomic dipole moment. The negative end of the dipole moment is better viewed as the donation of a mean negative electronic charge to the metal below. The positive end of the atomic dipole moment, is what has been called the net atomic charge  $Z_{eff}|e|$ .

The advantage to the dispersion method is that it fits smoothly into the power law limit of the well known Casimir force. In the density functional approach, the “image charges” are added in “by hand”. On the other

hand, the charge density functional approach is intuitive on a microscopic level.

The evidence for  $Z_{eff} > 0$  is based on the change in metallic work function due to adding submonolayer adatoms, for thicker films the situation is complex. [17] The work function can *increase* as the film thickness increases for film layers above the monolayer. This experimental fact has (thus far) no simple theoretical explanation.

## APPENDIX

In this appendix, the details of the mathematical derivation of results in Sec. V will be made explicit. One may define two projection operators  $\hat{Q}$  and  $\hat{P}$  obeying

$$\hat{Q} + \hat{P} = 1. \quad (A1)$$

The operator  $\hat{Q}$  projects a wave function onto the unperturbed ground state wave function  $\psi_0$  and may be written as

$$\hat{Q} = |\psi_0\rangle \langle \psi_0|. \quad (A2)$$

If we define for any operator  $\hat{A}$ , the projected operators  $A_{QQ} = \hat{Q}\hat{A}\hat{Q}$ ,  $A_{QP} = \hat{Q}\hat{A}\hat{P}$ ,  $A_{PQ} = \hat{P}\hat{A}\hat{Q}$  and  $A_{PP} = \hat{P}\hat{A}\hat{P}$ , then the operator may be written in a partitioned matrix form

$$\hat{A} = \begin{pmatrix} A_{QQ} & A_{QP} \\ A_{PQ} & A_{PP} \end{pmatrix}. \quad (A3)$$

In particular, the resolvent operator

$$\hat{\mathcal{R}}(z) = \left( \frac{1}{z - \mathcal{H}} \right) \quad (A4)$$

may be written as

$$\hat{\mathcal{R}}(z) = \begin{pmatrix} \mathcal{R}_{QQ}(z) & \mathcal{R}_{QP}(z) \\ \mathcal{R}_{PQ}(z) & \mathcal{R}_{PP}(z) \end{pmatrix}, \quad (A5)$$

where

$$G(z)1_{QQ} = \mathcal{R}_{QQ}(z) = 1_{QQ} \sum_n \frac{|(\Psi_n, \psi_0)|^2}{(z - \mathcal{E}_n)}. \quad (A6)$$

From Eq.(A6), it follows that  $G(z)$  has a ground state pole at  $z_0 = \mathcal{E}_0$  with a residue given by  $|(\Psi_n, \psi_0)|^2$ ; i.e.

$$G(z) \rightarrow \frac{|(\Psi_0, \psi_0)|^2}{(z - z_0)} \quad \text{as } z \rightarrow z_0. \quad (A7)$$

Eqs.(A4) and (A5) imply

$$\begin{pmatrix} z - \mathcal{H}_{QQ} & -\mathcal{H}_{QP} \\ -\mathcal{H}_{PQ} & z - \mathcal{H}_{PP} \end{pmatrix} \begin{pmatrix} \mathcal{R}_{QQ}(z) & \mathcal{R}_{QP}(z) \\ \mathcal{R}_{PQ}(z) & \mathcal{R}_{PP}(z) \end{pmatrix} \\ = \begin{pmatrix} 1_{QQ} & 0 \\ 0 & 1_{PP} \end{pmatrix}, \quad (A8)$$

from which

$$(z - \mathcal{H}_{QQ})\mathcal{R}_{QQ}(z) - \mathcal{H}_{QP}\mathcal{R}_{PQ}(z) = 1_{QQ}, \quad (\text{A9})$$

and

$$-\mathcal{H}_{PQ}\mathcal{R}_{QQ}(z) + (z - \mathcal{H}_{PP})\mathcal{R}_{PQ}(z) = 0. \quad (\text{A10})$$

Eqs.(A9) and (A10) imply

$$\left( z - \mathcal{H}_{QQ} - \mathcal{H}_{QP} \frac{1}{z - \mathcal{H}_{PP}} \mathcal{H}_{PQ} \right) \mathcal{R}_{QQ}(z) = 1_{QQ}. \quad (\text{A11})$$

Finally, if  $\mathcal{H} = H + V$ ,  $(\psi_0, V\psi_0) = 0$  and  $\mathcal{H}' = \mathcal{H}_{PP}$ , then Eqs.(A6) and (A11) read

$$\left\{ z - E_0 - \left( \psi_0, V \left\{ \frac{1}{z - \mathcal{H}'} \right\} V \psi_0 \right) \right\} G(z) = 1; \quad (\text{A12})$$

i.e.

$$G(z) = \left( \frac{1}{z - E_0 - \Sigma(z)} \right), \quad (\text{A13})$$

with a self energy

$$\Sigma(z) = \left( \psi_0, V \left\{ \frac{1}{z - \mathcal{H}'} \right\} V \psi_0 \right), \quad (\text{A14})$$

which completes our derivations.

- [14] T. Engel and R. Gomer, *it J. Chem. Phys.* **52**, 5572 (1970).
- [15] J.G. Dash, *Films on Solid Surfaces: The Physics and Chemistry of Physical Adsorption*, Academic Press, New York, (1975).
- [16] L.W. Bruch, M. Cole and E. Zaremba, *Physical Adsorption: Forces and Phenomena* Clarendon Press, Oxford (1997).
- [17] O. Yu Kolenychenko, O. I. Shklyarevskii, and H. van Kempen, *it Phys. Rev. Lett* **83**, 2242 (1999).
- [18] W. Widdra, P. Trischberger, W. Friess, D. Menzel, S. H. Payne, and H. J. Kreuzer, *Phys. Rev.* **B57**, 4111 (1998).
- [19] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics (Non-relativistic Theory)*, Page 135, Pergamon Press (Oxford) (1977).
- [20] L. D. Landau and E. M. Lifshitz, *op. cit.* Page 134.
- [21] H.B.C. Casimir, *Proc. R. Acad. Sci. Amsterdam* **60**, 793 (1948).
- [22] I.E.E. Dzaloshinski, E.M. Lifshitz and L.P. Pitayevski, *Advances in Physics* **10**, 165 (1961).
- [23] J. Harris and P.J. Feibelman, *Surf. Sci.* **115**, L133 (1982).
- [24] M.S. Tomassone and A. Widom, *Phys. Rev.* **B56**, 4928 (1997).
- [25] S. Rauber, R. Klein, M. Cole and L. W. Bruch, *Surf. Sci* **123**, 173 (1982).
- [26] W. Heitler, *Proc. Camb. Phil. Soc.* **37**, 291 (1941).
- [27] W. Heitler and H.W. Pang, *Proc. Camb. Phil. Soc.* **38**, 296 (1942).
- [28] N.D. Lang *Phys. Rev. Lett.* **46** 842 (1981).
- [29] N.D. Lang and R. Williams *Phys. Rev.* **B25** 2940 (1982).

- 
- [1] M.W. Roberts and C.S. McKee, *Chemistry of the Metal Gas Interface*, Chapt. 7, Oxford University Press, Oxford (1978).
  - [2] G. Vidali, G. Ihm, H-Y Kim and M.W. Cole, *Surf. Sci. Rep.* **12**, 133 (1991).
  - [3] E. Cheng, M.W. Cole, W.F. Saam and J. Treiner, *Phys. Rev.* **B48**, 18214 (1994).
  - [4] V. Pothier, C. Ramseyer, C. Girardet, V. Diercks, R. Halmer, R. David and P. Zeppenfeld *Phys. Rev.* **B57**, 13149 (1998).
  - [5] M. R. Trioni, S. Marcotulio, G. Santoro, V. Bortolani, G. Palumbo, and G. P. Brivio, *Phys. Rev.* **B**, 11043 (1998).
  - [6] W. Teizer, B. Hallock, E. Dujardin and T. W. Ebbesen, *Phys. Rev. Lett.* **82**, 5305 (1999).
  - [7] H. Lüth, *Surfaces and Interfaces of Solid Materials*, Chapt.9, Springer Verlag, Berlin (1995).
  - [8] J.C.P. Mignolet, *J. Chem. Phys.* **21**, 1298 (1953).
  - [9] J.C.P. Mignolet, *Disc. Faraday Soc.* **8**, 105 (1950).
  - [10] P.R. Antoniewicz, *Phys. Rev. Lett.* **32**, 1424 (1974).
  - [11] G. Ehrlich and F.G. Hudda, *J. Chem. Phys.* **30**, 493 (1959).
  - [12] J. Van Oirschot and W.M.H. Sachtler, *Ned. Tijdschr. vac. Tech.* **8**, 96 (1970).
  - [13] A.M. Chesters and J. Pritchard, *Surf. Sci.* **35**, 161 (1973).